[CONTRIBUTION FROM THE MELLON INSTITUTE, PITTSBURGH, PA]

Chemisorption of Nitrogen on Nickel Catalysts

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It has been shown that both pure nickel catalysts and those promoted with small amounts of silica will chemisorb nitrogen to a slight extent at about 250 to 300°. Moreover, at least in the case of the pure nickel catalysts, a different type of chemisorption occurs at −195°. The amounts chemisorbed at high temperatures for the pure nickel cataylst correspond to 5% surface coverage calculated as molecular nitrogen. The low temperature chemisorption corresponds to as much as 28% surface coverage. The nitrogen adsorbed at −195° is removed easily by evacuation at room temperature and is almost completely blocked out by the presence of chemisorbed nitrogen put on at high temperatures. In addition, the amount of nitrogen adsorbed at −195° (expressed as fractional surface coverage) is very sensitive to the previous history of the catalyst.

On thin metal films both Beeck[2] and Trapnell[3] have noticed a considerable amount of nitrogen chemisorption at −195°. This has not so far been reported for nickel catalysts formed by reduction of the oxide. In view of the wide use that is made of nitrogen adsorption at −195° for measuring the surface area of metals and other solids, it seemed worthwhile to ascertain whether or not nitrogen chemisorption at this low temperature could be detected.

Experimental

Both promoted and unpromoted catalysts were used in these studies. The unpromoted catalysts, which will be referred to henceforth as pure nickel, were prepared from a solution of low cobalt $Ni(NO_3)_2 \cdot 6H_2O$. Solid NH_4HCO_3 was added to this solution to form the basic nickel carbonate which was then calcined to NiO and reduced. Two batches of pure nickel catalyst were prepared. In preparation A the basic carbonate was calcined in a muffle furnace at 400° for 6 hr. In B, the calcination was carried out at 450–475°. Otherwise the procedure used for batch B was the same as that used for A. This is essentially the same procedure used by Best and Russell[4] and by Hall and Alexander.[5] Two samples of catalyst from each preparation were studied. Samples AI, AII and BII were reduced in hydrogen purified by passage over hot Cu and through a trap containing activated charcoal at −195°. This purification should assure that the hydrogen was free from oxygen, water vapor and nitrogen. These samples were reduced at 325 to 330° at a space velocity of 2500 to 3000 hr.$^{-1}$ for at least 20 hr. Sample BI was reduced at 315° for 8 hr. In this case, however, the hydrogen was purified by passage over hot Cu and through an *empty* trap at −195°. Thus, the hydrogen used for the reduction of sample BI probably contains some nitrogen. In every case at the end of the reduction the exit gas contained less than 0.002% water. The weight loss for the air-dry NiO in a typical reduction was 23.55% (compared to a theoretical value of 21.42% for pure dry NiO). Analysis indicated that the air-dry sample contained 76.7% Ni. In all cases these reduced catalysts were evacuated 1–2 hr. at the reduction temperature prior to the start of the adsorption experiments.

The other type of catalyst used in the present studies was pelleted NiO promoted with less than 1% SiO_2 and containing a small amount of graphite as a lubricant for pelleting. A sample of this catalyst (14.83 g.) was reduced in hydrogen for 48 hr. at 300° at a space velocity of 1000 hr.$^{-1}$. In the last 20 hr. of the reduction, the tail gas contained 0.01 to 0.02% water. Before the start of the chemisorption experiment the catalyst was further reduced for 2 hr. at 310° and a space velocity of 5000 hr.$^{-1}$ and then evacuated for 16 hr. at the reduction temperature. The hydrogen was purified by passage through a Deoxo unit and an empty trap at −195°.

Results and Discussion

Figure 1 shows the principal features of an adsorption isobar on the promoted Ni catalyst. The complete results for experiments on the promoted catalyst are summarized in Table I in the order in which they were obtained.[6] From Table I the total surface area of this sample may be roughly estimated as about 340 m.^{2} (23.0 m.^{2}/g. of unreduced catalyst); furthermore, the data of the table show that at a given temperature little or no creep was observed in the adsorption points below the reduction temperature. The isobar in Fig. 1 is typical for systems in which activated adsorption is occurring. The amount of adsorbed nitrogen decreases with increasing temperature, passes through a minimum value (essentially zero) at 433°K. and then increases at higher temperatures. This can be taken as evidence for activated adsorption or chemisorption of the nitrogen taking place above 433°K. The amount of such chemisorption corresponds to roughly 1% coverage of the total surface if the adsorbed nitrogen is assumed to be molecular. Needless to say, this may correspond to a much higher coverage of the metallic nickel surface since in a promoted catalyst only a fraction of the surface is made up of the pure metal, the remainder being covered with promoter. From the data available for this sample it is not possible to state definitely whether or not the adsorption below 400°K. is all physical or a mixture of physical and chemical though measurements described below for the pure nickel catalyst suggest that at least part of the adsorption at 200°K. on the Ni–SiO_2 sample is a low temperature chemisorption.

After the results summarized in Table I and Fig. 1 were obtained the temperature of the catalyst was maintained at 633°K. for several hours. At this temperature, which is above the reduction temperature (583°K.), the catalyst degassed slowly. This was evidenced by an increase in the amount of gas present to a point where it was about 0.5 cc. greater than the amount of nitrogen originally introduced. The temperature then was dropped to below the reduction temperature and the nitrogen pressure was increased 15-fold in an effort to see whether the amount of nitrogen chemisorption

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[1] Loyola College, Baltimore, Maryland.

[2] Beeck, "Advances in Catalysis," Vol. II, Academic Press, Inc., New York, N. Y., 1950, p. 155.

[3] Trapnell, *Proc. Roy. Soc.* (*London*), **A218** 566 (1953).

[4] Best and Russell, THIS JOURNAL, **76**, 838 (1954).

[5] W. K. Hall and Leroy Alexander, *J. Phys. Chem.*, **61**, 242 (1957).

[6] This sample was not cooled in He to −195° prior to the start of the adsorption experiment. After 16 hr. evacuation at 310°, it was cooled to room temperature and thoroughly evacuated, then cooled *in vacuo* to −195°. After about 20 min. at this temperature the nitrogen was admitted; thus, the initial nitrogen adsorption took place on a catalyst which was probably at a temperature somewhat above −195° but considerably below room temperature.

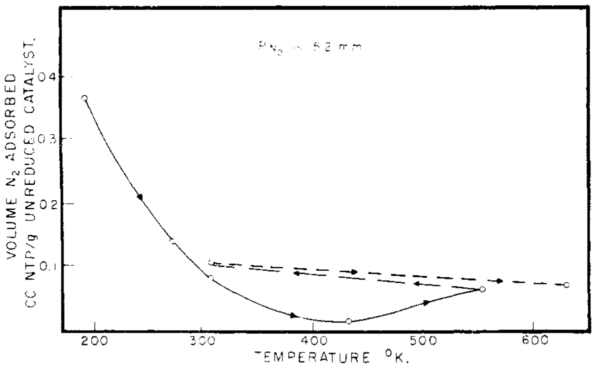

Fig. 1.—Nitrogen isobar on a reduced promoted nickel catalyst (14.8 g. as oxide).

could be increased by exposure of the catalyst to nitrogen at higher pressures. After exposure of the catalyst to nitrogen at 730 mm. for three days at 557°K. no appreciable increase in nitrogen chemisorption occurred.[7] If during the reduction nitrogen chemisorption occurred owing to the trace amounts of nitrogen in the hydrogen stream, subsequent experiments dealing with nitrogen chemisorption would, at best, give only qualitative results. In an effort to check this point the catalyst, after the above mentioned exposure to nitrogen, was degassed at 770°K. for roughly 75 hr. The evolved gas (~ 35–40 cc.) was analyzed by the mass spectrograph and consisted of H_2, H_2O, CO and CO_2 in addition to nitrogen. The amount of nitrogen evolved corresponded, within experimental error, to the amount introduced in the adsorption experiments. It is likely, therefore, that during the reduction of this catalyst with hydrogen containing traces of nitrogen little chemisorption of nitrogen occurred. The fact that H_2, H_2O, CO and CO_2 were present in the evolved gas is of interest for several reasons. If all of the hydrogen came from hydrogen chemisorbed during the reduction, the surface was at least 30–40% covered with hydrogen even after 16 hr. evacuation at the reduction temperature (310°). The fact that oxygen still was present even after the reduction is actually not surprising. Recent work carried out by van Eijk, van Voorthuijsen and Franzen[8] indicated that nickel catalysts supported on SiO_2 are quite difficult to reduce. Furthermore, they contend that at high temperatures diffusion of H_2O out of the SiO_2 will slowly oxidize the metallic surface of reduced catalysts.[9] Apparently the H_2O initially degassed reacts with the graphite binder to form CO, CO_2 and hydrogen. Then, the metallic nickel acts as a catalyst for the water gas reaction. Analysis of the gases, at the conclusion of this experiment, showed that the water gas equilibria was attained.

TABLE I

NITROGEN ADSORPTION ON PROMOTED Ni CATALYSTS (14.8 G. BEFORE REDUCTION)

Temp., °K.	Cc. NTP adsorbed/g. unreduced catalyst	Equilibration time (min.)	P, mm.
78	5.27	20	55
195	0.38	35	54
195	.365	240	56
273	.135	68	48
308	.081	12	52
433	.007	10	51
433	.007	30	52
557	.061	480	55
556	.061	600	54
308	.102	150	53
633	.068	30	52

Results with the pure nickel catalysts are summarized in Table II. Figure 2 shows the plots of the first four nitrogen isotherms obtained for sample A at −195° with various pretreatments and Fig. 3 shows a nitrogen isobar between 200 and 600°K. The specific surface of catalyst A in these runs was about 2 m.²/g. of unreduced catalyst.

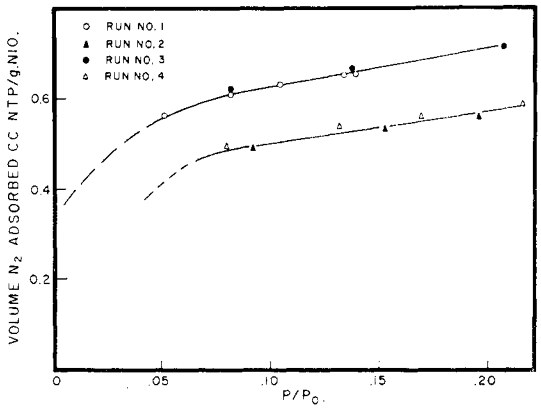

Fig. 2.—Adsorption of nitrogen on a reduced pure nickel at −195° (21.0 g. as oxide).

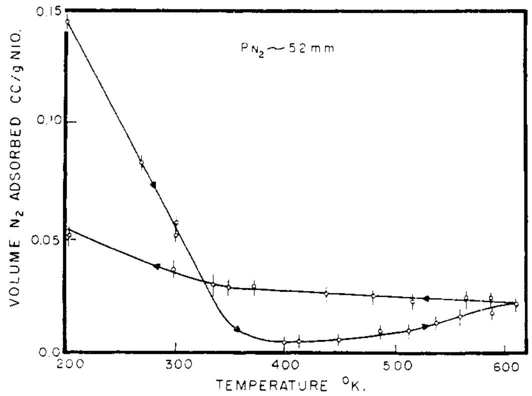

Fig. 3.—Nitrogen isobar on a reduced pure nickel catalyst (21.4 g.)

After the standard evacuation for 2 hr. at the reduction temperature the reduced catalyst was cooled in He to −195°. The sample was evacuated and the isotherm designated as run no. 1 was obtained. After completion of this run, the catalyst was then evacuated for several minutes at −195° and for 1 hr. at −78°. At this point, the evacua-

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[7] This can also be taken as strong evidence that the nitrogen was not contaminated with oxygen.

[8] van Eijk, van Voorthuijsen and Franzen, *Rec. trav. chim.*, **70**, 793 (1951).

[9] Schuit and De Boer, *ibid.*, **70**, 793 (1951).

tion was stopped and the sample was cooled to −195° in He and evacuated for 10 to 20 minutes. Then the second isotherm was determined. The difference between runs no. 1 and 2 clearly shows that part of the nitrogen adsorbed at −195° is not removed by evacuation at −78°. Since physical adsorption is usually removed by this treatment, it appears that the chemisorption of nitrogen is occurring at low temperatures. We shall refer to this as L. T. nitrogen chemisorption. After evacuation of the catalyst for 16 hr. at room temperature, the procedure was repeated (runs no. 3 and 4). The L. T. nitrogen is apparently weakly bound to the surface since evacuation at room temperature will remove it and restore the catalyst to substantially its original state. This observation is consistent with the results obtained by Beeck[2] and Trapnell[3] for thin metal films. In view of this, it is quite likely that some of the low temperature chemisorbed nitrogen is pumped off even at −78°. Therefore, the difference in adsorption between runs 1 and 2 (or 3 and 4) should be regarded as minimum values for L. T. nitrogen chemisorption. This corresponds to a minimum coverage[10] of 28% if the adsorbed gas is assumed to be molecular in form. Actually, because of the apparent weakness of the nitrogen–nickel bond it seems quite likely that the adsorption occurs as molecular nitrogen rather than as atoms.

Table II

Adsorption of Nitrogen on Pure Nickel Formed by Reduction of Nickel Oxide

Run no.	Pretreatment	Vm,[a] cc./g. oxide	[a]V[b] chemisorbed, cc./g. oxide
	Catalyst A, sample I, pure Ni (21.0 g. oxide)		
1	Initial reduction	0.586[c]	
2	1 hr. −78° pumpout	.462	0.133
3	16 hr. 35° pumpout	.571[c]	
4	1 hr. −78° pumpout	.476	.133
	Catalyst A, sample II, pure Ni (21.4 g. oxide)[d]		
7	Overnight evacuation, regenerative reduction	0.533[c]	
8	1 hr. −78° pumpout	.467	0.093
9	16 hr. 30° pumpout	Isobar see Fig. 3	
10	End of isobar, no evacuation	0.388[c,f]	
11	1 hr. −78° pumpout	.365[g]	.037[f]
12	20 hr. 30° pumpout	.372[c,g]	.009[g]
13	Regenerative reduction	.462[c]	
14	1 hr. −78° pumpout	.420	.061
15	Regenerative reduction	.439[c]	
16	1 hr. −78° pumpout	.402	.051
17	Raised temp. to 320° in presence of (h) N_2		.037[i]
18	1 hr. 30° pumpout	.374[c,g]	
19	1 hr. −78° pumpout	.374[c]	
20	Regenerative reduction	.425[c]	
21	1 hr. −78° pumpout	.384	.057
22	1 hr. 30° pumpout	.425[c]	.057
	Catalyst B, sample I, pure Ni (25.8 g. oxide)		
23	Initial reduction	0.388[c]	
24	1 hr. −78° pumpout	.337	0.064
25	16 hr. evacuation at 30°	.388[c]	
26	1 hr. −78° pumpout	.341	.064
27	Heated in N_2 1 hr. 309° evacuated 1 hr. 309°	.348[c]	
28	1 hr. −78° pumpout	.330	.027
29	Rereduced 1 hr. 300°	.330[c]	
30	−78° evacuation	.302	.050
	Catalyst B, sample II, pure Ni (24.2 g. oxide)		
31	Initial reduction	0.239[c]	
32	1 hr. −78° pumpout	.223	0.019
33	16 hr. 30° pumpout	.239[c]	
34	Exposed to air at 300° rereduced	.131[c]	
35	1 hr. −78° pumpout	.127	.007

[a] V_m was calculated using the BET equation. The partial pressure at which V_m occurs depends on the nature of the surface of the adsorbent. If chemisorbed N_2 is present (*e.g.*, in runs where the catalyst has been exposed to N_2 at −195° and evacuated for 1 hr. at −78°) the V_m occurs at a higher partial pressure of N_2 than with a clean catalyst. Thus, the values in column 4 are in general greater than the difference between the corresponding V_m values. [b] V chemisorbed is defined as the volume of N_2 adsorbed at −195° that is not removed by evacuation for 1 hr. at −78° when one starts with a clean catalyst. Evacuation at room temperature does remove this chemisorbed N_2. Thus V chemisorbed can also be defined as the amount of N_2 adsorbed at −195°, that is not removed by evacuation at −78° but is removed by room temperature evacuation. These methods apply only to chemisorption at low temperatures. [c] These values, of course, include some chemisorbed N_2. The calculated values of V_m using the BET equation are meant to serve only as an indication of the extent of chemical plus physical adsorption. [d] Prior to run no. 7 this catalyst was reduced in the standard fashion and used for N_2 and CO adsorption studies. The regenerative reduction (2 hr. additional reduction under standard conditions plus 2 hr. evacuation) was found to restore the catalyst to its initial condition in earlier work with CO and N_2 adsorption studies. [f] The volume of high temperature N_2 chemisorption is included in these values. [g] The volume of high temperature N_2 chemisorption is not included in these values. [h] In this run the catalyst was heated to 320° with N_2 (∼600 mm.) for 16 hr. [i] This is the amount of N_2 adsorption at 320°. It is, of course, a chemical type of adsorption.

Several CO chemisorption runs (to be presented in a later paper) were made on the freshly reduced catalyst AII prior to the experiments summarized in Table II. Immediately before run no. 7 the catalyst was rereduced 2 hr. at 325° and evacuated for 2 hr. at the reduction temperature. Previous work in this Laboratory has shown that this restores the catalyst to its original condition. Runs 7 and 8 provide a qualitative check on the low temperature chemisorption. The quantitative agreement with the runs for sample AI is not good. In this case the low temperature chemisorption of nitrogen covers at least 20% of the surface compared to 28% for sample AI. This difference, which is well outside the assumed experimental error, will be discussed later in connection with Table II.

After the catalyst was evacuated for 16 hr. at room temperature, the isobar shown in Fig. 3 was obtained. The order in which the experimental points were obtained is indicated by the arrows. The points obtained on increasing the temperature will be referred to as the "ascending branch" of

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(10) The apparent per cent. coverage given here is a minimum both because the chemisorption value of 0.133 cc. may be smaller than the true chemisorption and because, due to a partial removal of some chemisorption during the evacuation at −78°, V_m for physical adsorption may be a little smaller than the figures 0.462 and 0.476 given in Table II.

the isobar. Those obtained on decreasing the temperature will be referred to as the "descending branch." The amount of nitrogen adsorbed at 200°K. (ascending branch) clearly shows the presence of L. T. nitrogen chemisorption. At this temperature the total adsorption corresponds to nearly 32% of the total surface. Roughly speaking, only a few per cent. surface coverage by physical adsorption would be expected to occur at Dry Ice temperatures at these pressures. On this basis the amount of chemisorbed nitrogen could amount to as much as 30% of the surface. On the other hand, run 8 Table II leads to an estimate of about 20% coverage by chemisorbed nitrogen. Thus, it appears that some of the L. T. nitrogen chemisorption may be removed by evacuation at $-78°$. The amount of nitrogen chemisorbed at room temperature corresponds to 12 to 13% coverage of the surface. Once again, one would expect less than 0.5% coverage due to physical adsorption of nitrogen at these pressures. Above room temperature, the total amount of nitrogen chemisorption drops on the ascending branch, becoming essentially zero at 400°K. When the temperature is further increased, the adsorption increases, indicating that a second type of chemisorption is occurring. (This adsorption at high temperature will be designated as H. T. nitrogen chemisorption.) The amount of H. T. chemisorption increases up to the temperature at which the reduction was carried out and reaches a value corresponding to 5% surface coverage calculated as molecular nitrogen. The descending branch shows the hysteresis typical of chemisorption until a temperature slightly above 320°K. is reached. Normally, one would expect the adsorption on the descending branch to lie wholly above that for the ascending branch since the irreversibly adsorbed H. T. nitrogen chemisorption should not affect physical adsorption. In the present instance, the two branches cross and at 200°K. the adsorption for the descending branch is only about $^1/_3$ that found for the ascending branch. Two possible explanations of this crossover are: (1) sintering occurs at 600°K. to such an extent that $^2/_3$ of the surface area is lost. (2) The H. T. nitrogen chemisorption ($\sim$0.03 cc./g.) blocks out almost completely the chemisorption of nitrogen ($\sim$ 0.10 cc./g.) at 200°K. Runs 10 through 16 clearly show the latter of these two explanations is applicable. The *total* chemisorption (*i.e.*, that which is not removed by evacuation for 1 hr. at $-78°$ in runs 10 and 11) is 0.037 cc./g. Roughly 0.03 cc./g. of this is H. T. nitrogen chemisorption; hence only about 0.007 cc./g. is L. T. chemisorption. This is borne out by run no. 12 which shows that the amount of chemisorbed nitrogen removed by evacuation at room temperature (*i.e.*, L. T. nitrogen chemisorption) is only 0.009 cc./g. Runs 13 through 16 show that in a qualitative sense the catalyst is largely returned to its initial condition by regenerative reduction. Furthermore, if we attribute the differences found between runs 13 and 15 to sintering during the regenerative reduction, we can estimate the loss of surface area due to sintering during the isobar. On this basis, the decrease in surface area would be less than 10%. Thus, the sintering that occurs during the isobar cannot explain the crossing of the ascending and descending branches of the isobar.

Further evidence that H. T. nitrogen chemisorption blocks out L. T. nitrogen chemisorption was obtained in runs 17 through 22. In run 17 the catalyst was heated in nitrogen at 320° for 16 hr. The nitrogen pressure was more than ten-fold that used for the isobar. If we assume there was no degassing of the catalyst 0.037 cc. of nitrogen was chemisorbed. The catalyst was then evacuated at 30° which would remove any L. T. nitrogen chemisorption and runs 18 and 19 carried out. It is apparent that the H. T. nitrogen chemisorption was increased by the higher pressure (and perhaps longer contact time) in run no. 17. This increase was apparently sufficient completely to block out the L. T. nitrogen chemisorption. Once again, the catalyst is restored to roughly its initial conditions by regenerative reduction. Runs 20 through 22 show this clearly. Incidentally, it is of some interest to note that sintering which occurred in runs 15 through 20 was considerably less than that for runs 7 through 13. This is in line with the general observation that the rate of sintering at a given temperature falls off with increasing time of exposure.

Runs 23 through 35 in Table II were all carried out with samples from preparation B of the pure Ni catalyst. Runs 23 through 30 were carried out to see what effect, if any, the traces of nitrogen in the hydrogen reducing stream had on the nitrogen chemisorption results. To this end, the initial reduction on sample BI was carried out with hydrogen purified by passage over hot Cu and through an *empty* trap at liquid nitrogen temperatures. Moreover, as already noted, the reduction schedule was somewhat milder than in previous runs. Runs 23 through 26 clearly show that this catalyst is quite similar to catalyst A. The surface area is somewhat lower but this effect probably is due in part to the higher calcination temperature in its preparation. On the freshly reduced catalyst the L. T. nitrogen chemisorption covers about 19% of the surface, and, as in the case of catalyst A, this nitrogen is completely removed by room temperature evacuation. The catalyst was then exposed to nitrogen at 309°, evacuated for 1 hr. at this temperature and cooled to $-195°$ in helium. Then, runs 27 and 28 were carried out. A small amount of sintering occurred due to this heating but even more striking was the reduction in the amount of L.T. nitrogen chemisorption. In the case of catalyst A, H. T. nitrogen blocked but almost completely the L. T. nitrogen. In the present case the L. T. nitrogen was reduced to 40% of its former value by exposure of the catalyst to nitrogen at 309° plus 1 hr. evacuation at this temperature. These results imply that only part of the H. T. nitrogen chemisorption was removed by the evacuation at elevated temperatures. At this point the catalyst was evacuated at room temperature for 1 hr. to remove L. T. nitrogen and rereduced with nitrogen-free hydrogen. The tail gas was passed through a liquid nitrogen trap. After 1 hr. the trap was found to contain a trace of NH_3, which definitely shows that not all of the H. T. nitrogen was removed by evacuation. After this reduction the catalyst, although somewhat sintered, was returned substantially to its initial state insofar as the L. T. nitrogen chemisorption (runs 29 and 30) covered about 16% of the surface compared to 19% for the virgin catalyst.

A second sample of catalyst B was reduced with the same procedure used for catalyst A. Runs 31 through 33 show that in a qualitative sense this catalyst shows the same type of L. T. nitrogen chemisorption as was found for catalyst A. In a quantitative sense, however, two striking differences were observed. Firstly, catalyst BII had less than half the surface area (V_m) found for a virgin sample of catalyst A. This difference could easily be due to the higher calcination temperature used in its preparation. Even more striking is the fact that the fractional coverage of the surface with L. T. nitrogen apparently is only 0.09 with this catalyst. In an effort to see whether there were any correlation between the surface area and the extent of L. T. nitrogen chemisorption this catalyst was exposed to air at 300° and then rereduced. The results of runs 34 and 35 clearly show that not only was the specific surface reduced by this procedure, but, as suspected, the extent of L. T. nitrogen chemisorption also fell off. This effect appears to be quite general for a given nickel catalyst. In Table III we have listed the values of θ for L. T. nitrogen and the V_m after a $-78°$ evacuation. It is quite clear that there is a definite trend for θ L. T. nitrogen, as *defined*, to fall off as the V_m decreases for a given catalyst preparation. In actual fact the data in Table III do not require that the fractional surface coverage by the chemisorption of nitrogen at low temperature change with sintering. Since all of the chemisorbed nitrogen is removed by room temperature evacuation it is not unlikely that part of it is removed by evacuation at $-78°$. This would mean that if a decrease in the heat of chemisorption accompanied the sintering one would find an apparent decrease in the value of θ L. T. nitrogen while the actual fractional coverage of the surface with chemisorption at $-78°$ would remain unchanged. Both of these interpretations seem reasonable. The sites at which nitrogen chemisorption occurs could be points of high activity due to slight defects in surface structure. Sintering of the catalyst would probably decrease this lack of register which would result in a decrease in the heat of adsorption at these points. On the other hand, the sintering could also remove completely some of the defects which would lead to a decrease in the extent of L. T. nitrogen chemisorption. If either or both of these possibilities occur the data in Table III would be expected and the question as to whether or not chemisorption occurred on nickel catalysts at liquid nitrogen temperatures could depend not only on the criteria for chemisorption but also on the history of the nickel sample.

Table III

Sample	V_m, cc./g.[a]	θ L. T. N_2[b]
AI	0.476	0.28
AII	.467	.20
AII	.420	.15
AII	.402	.13
AII	.384	.15
BI	.337	.19
BI	.302	.16
BII	.223	.09
BII	.127	.06

[a] These are the V_m values found after the $-78°$ evacuation following the determination of the initial N_2 isotherm. [b] These values were calculated assuming the chemisorption took place as molecular N_2 with the same cross sectional area as physically adsorbed N_2. θ is the fraction of the surface covered by chemisorbed nitrogen.

The present data are too incomplete for speculation as to the types of bonding involved in the two types of nitrogen chemisorption. The data in Table II are not inconsistent with the possibility that L. T. nitrogen is molecular and H. T. nitrogen is atomic if both take place on the same sites. (The ratio of the former to the latter approaches 2:1.)

Recently Selwood, *et al.*,[11] found that nitrogen adsorbed on nickel at high temperatures increased the magnetization of the nickel. On the basis of this result, he postulated that nitrogen extracted electrons from the d-band of the metal to form a chemisorption bond with the metal. More recently, Broeder, *et al.*,[12] have shown that this effect is not obtained unless the surface of the metal is partially covered with hydrogen. The authors, in fact, suggest that the nitrogen flushing merely removes the chemisorbed hydrogen (which decreases the magnetization) and then the observed increase in magnetization occurs. An alternative interpretation of these results would be that the adsorption of nitrogen by nickel will occur only in the presence of hydrogen. In view of this possibility it should be kept in mind that the results herein reported were carried out on catalysts which may have contained some chemisorbed hydrogen in spite of the high temperature evacuation which preceded each run.

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[11] Selwood, Adler and Phillips, This Journal, **76**, 2281 (1954).

[12] Broeder, Van Reijen and Korswagen, *J. chim. phys.*, **54**, 37 (1957).